California Regional PM_{10} and $PM_{2.5}$ Air Quality Study (CRPAQS)

Statement Of Work – CRPAQS Data Analysis Task 1.1b
EXAMINATION OF THE REACTIVE NITROGEN PARTITIONING AT THE BAKERSFIELD AND ANGIOLA FIELD SITES.

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Introduction

Previous studies have indicated that, under many conditions, formation of aerosol nitrate in the San Joaquin Valley (SJV) depends on the availability of nitric acid. In turn, the formation of nitric acid depends on both the availability of precursors and the oxidative capacity of the atmosphere. This data analysis task is aimed at bettering our understanding of the reactive nitrogen partitioning observed during the CRPAQS measurement phase and relating variations in that partitioning to the coincident oxidative conditions. One of the first steps in this analysis is to assess the reliability of the various NO_y components (NO, NO_2, PAN, HNO_3, and particulate nitrate, [collectively $NO_{y(i)}$]) that were measured. At this time, it is understood that PAN data will be available for a limited number of episodes and that HNO_3 data is not available from the Angiola core site. In addition, the NO_2 data that is available is limited in temporal coverage. Further analysis will incorporate other chemical and physical parameters as needed to generate a better understanding of the conditions that lead to formation of nitric acid and subsequently the formation of particulate nitrate. It is expected that the conditions identified will vary as a function of atmospheric conditions (e.g., fog versus no fog).

The objectives of this work are to address the following questions for the reactive nitrogen species:

1. What is the comparability and equivalence among collocated sampling methods, what are the biases of one instrument with respect to others, and how should these biases be minimized?
2. What is the quality of the NO_y and $NO_{y(i)}$ species data collected? If some bias in the data is found, what utility might the data still have (e.g. establishing limits on the concentration of some species)?
3. How do the established data quality bounds limit the utility of the reactive nitrogen data to illustrate the chemical and physical processes that link the primarily gas-phase reservoir of reactive nitrogen to particulate matter (PM) concentration issues?

Technical Approach

Continuous measurements of NO_y and a number of nitrogen species components were made at the anchor sites during the CRPAQS winter measurement periods. We will evaluate these measurements and characterize the partitioning among these species by making various comparisons as a function of site, time of day, and meteorological characteristics. Previous studies have indicated that under many conditions, formation of aerosol nitrate in the SJV depends on the availability of HNO_3. In turn, the formation of nitric acid depends on both the availability of precursors and the oxidative capacity of the atmosphere. This data analysis task is aimed at evaluating and documenting the quality of the reactive nitrogen species measurements and improving our understanding of the reactive nitrogen partitioning observed during the CRPAQS measurement phase and relating variations in that partitioning to the coincident oxidative conditions.

Results of this task will serve to establish confidence limits on the evaluation of processes leading to the formation of particulate nitrate from its precursor species. Additional value will be realized by generation of a quality-assured NO_x/NO_y ratio parameter, which has good utility as an air mass age indicator.

<u>Data Availability</u>

Continuous air quality data was collected for a number of reactive nitrogen species at the anchor sites during the winter measurement periods, typically mid-November 2000 through mid-February 2001 (see **Table 1**). These measurements include NO_y and its major components NO, NO_2, PAN, nitric acid, and aerosol nitrate. All these measurements were made at a time resolution of 5 or 10 minutes (see **Table 2**). Tables 1 and 2 also show the data availability and time resolution of several additional parameters that might influence the nitrogen species partitioning, including ozone, $PM_{2.5}$ and PM_{10} mass, light scattering, and black carbon. Evaluation of the reactive nitrogen budget will require integration of the NO, NO_2, HNO_3, and NO_y measurements over the sample period of the nitrate measurement. When we compare the nitrogen species concentrations or partitioning with PM mass measurements, we will have to average the data to 60-minute time periods.

Table 1. Continuous nitrogen species measurements (and selected other continuous measurements) made at the Angiola, Bakersfield, Fresno, Bethel Island, and Sierra Nevada Foothills sites.

ID	Site Instrument	Angiola	Bakersfield	Fresno First Street	Bethel Island	Sierra Nevada Foothills
A	Nephelometer	2/1/00–2/16/01	1/27/00-4/18/01	12/1/99-2/1/01	11/15/00-2/15/01	11/2/00–2/8/01
G	Aethalometer	1/12/00–3/29/01	1/20/00-2/19/01	12/1/99-2/1/01	11/17/00-2/15/01	11/19/01–2/14/01
J	PM_{10} BAM	1/21/00–3/29/01	1/21/00-4/9/01	12/1/99-2/1/01	Ongoing (BAAQMD)	11/19/01–2/12/01
K	$PM_{2.5}$ BAM	1/21/00–3/29/01	1/21/00-4/18/01	12/1/99-2/1/01	11/17/00-2/15/01	11/19/01–2/12/01
N	PAN/NO_2	11/19/00–2/12/01	10/11/00-2/12/01	12/10/00-2/1/01	11/22/00-2/12/01	11/10/00–2/13/01
O	NO_y	12/20/99–2/23/01	12/16/99-3/26/01	12/1/99-2/1/01	11/18/00-2/15/01	11/16/00–2/15/01
P	O_3	1/22/00–2/21/01	Ongoing (ARB)	Ongoing (ARB)	Ongoing (BAAQMD)	11/3/00–2/13/01
Q	Nitrate	11/19/00–3/2/01	11/15/00-3/6/01	11/13/00-2/101	11/28/00-2/6/01	11/20/01–2/12/01
R	HNO_3	11/21/00–2/26/01	–	11/30/00-2/1/01	–	11/16/00–2/15/01

Table 2. Time resolution of continuous nitrogen species measurements (and selected other continuous measurements) made at the Angiola, Bakersfield, Fresno, Bethel Island, and Sierra Nevada Foothills sites.

ID	Instrument	Time resolution (minutes)
A	Nephelometer	5, 60
G	Aethalometer	5, 60
J	PM_{10} BAM	60
K	$PM_{2.5}$ BAM	60
N	PAN/NO_2	5, 60
O	NO_y	5, 60
P	O_3	5, 60
Q	Nitrate	10, 60
R	HNO_3	5, 60

Data Validation and Evaluation Process

We are assuming that all the data in the CRPAQS database will have undergone Level I validation. In brief, Level I validation consists of eliminating known invalid data, flagging anomalous data, replacing missing data with backup data in the event of a failure of the primary system, and applying adjustments based on calibrations or known interference. Level II sample validation applies consistency tests based on known physical relationships between variables to the assembled data. We will perform Level II validation checks in the initial phases of the data analysis. Level III sample validation is part of the data interpretation process and involves further investigation of measurements that may seem inconsistent with physical expectations. We will perform Level III validation checks whenever the need arises during our data analyses.

The Level II validation tasks will be based on either direct or inferential consistency checks. Direct checks can be performed where we have collocated measures of the same species. This is possible for NO_y at three of the anchor sites (Fresno First Street, Angiola, and Sierra Nevada Foothills). Remaining consistency checks will depend on inferential evaluation based on the ratios NO/NO_2, NO_x/NO_y, $NO_{y(i)}/NO_y$, and $\Sigma NO_{y(i)}/NO_y$ (where $NO_{y(i)}$ refers to the individual NO_y components measured: NO, NO_2, PAN, HNO_3, and NO_3^-).

One of the first steps in this analysis is to make an assessment of the reliability of the NO_y measurements. For example, we will compare the NO_y measured by the NO/NO_y monitor with the NO_y measured by the nitric acid monitor (this is a Level II data validation check). Consistency between these two NO_y measurements will promote confidence in the nitric acid measurements. An example scatter plot of 5-minute NO_y data collected by the two different monitors at the Sierra Nevada Foothills site on December 28, 2000, is shown in **Figure 1**. Note that the two NO_y measurements are almost identical; this demonstrates that the two separate monitors were operating in a consistent manner. We will conduct additional NO_y comparisons for each site and for various times during the CRPAQS winter measurement periods to evaluate the comparability of the two NO_y measurements. Any bias discovered between the collocated measurements of NO_y will help to establish uncertainty bounds for subsequent evaluation of the reactive nitrogen budget.

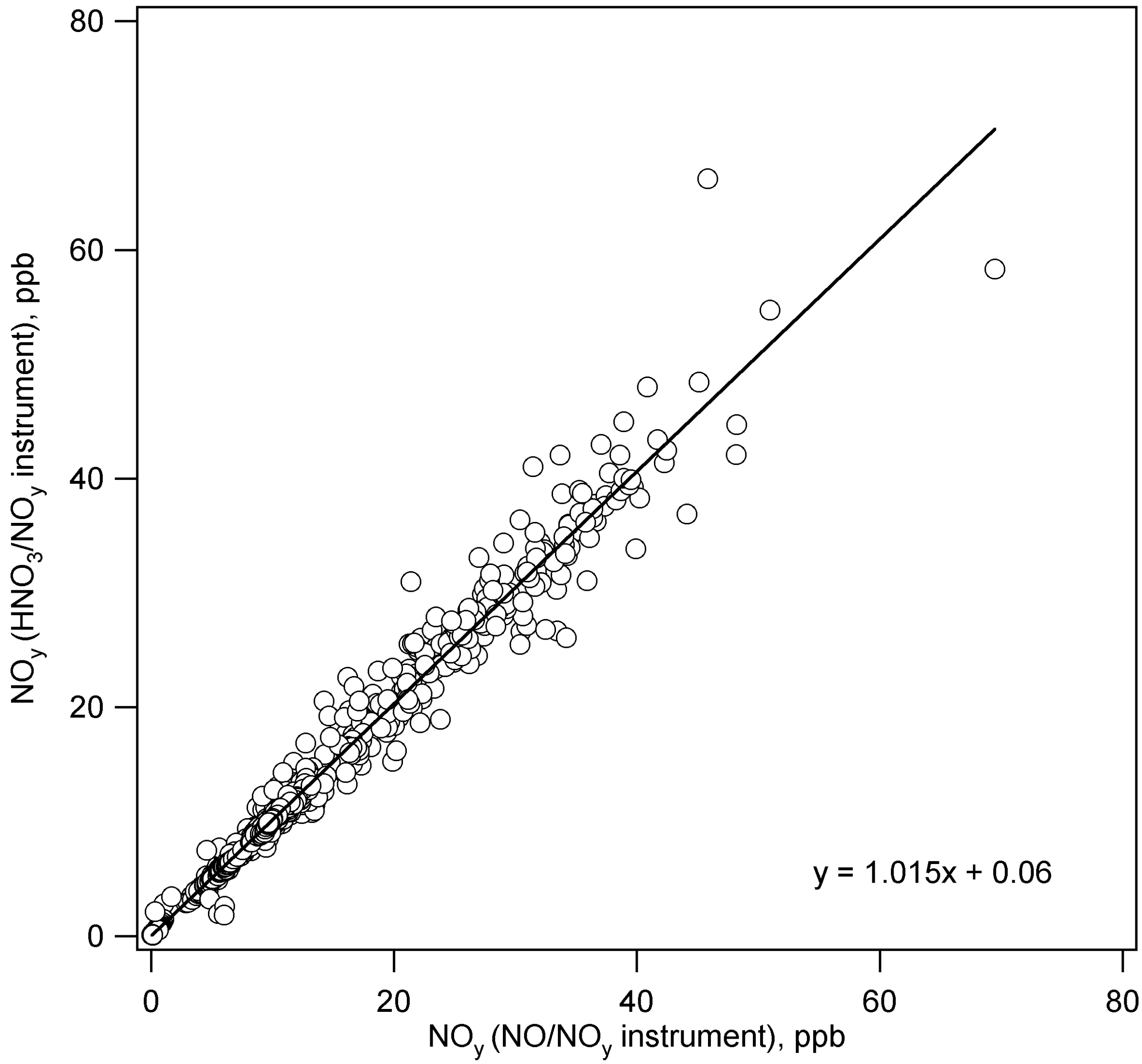

Figure 1. Scatter plot of 5-minute data from the two NO_y measurements collected at the Sierra Nevada Foothills site on December 28, 2000. These measurements show excellent agreement, which provides confidence in the NO_y measurement to be used as the conserved quantity in subsequent evaluation of the reactive nitrogen budget.

The reactive nitrogen reservoir is replenished in the form of NO_x (NO +NO_2), which necessitates good NO_x measurements for any study of reactive nitrogen chemistry. The next step is to evaluate the NO_x data quality. This is a significant task because NO and NO_2 were measured with different types of instruments, which may lead to different biases in the NO_x quantity as a function of concentration. In Task 1.1b, the first step is to examine the time series available for both measurements and assess whether adjustments need to be made to one or both measurement records to account for differences in timing or response speed. Assuming that any differences discovered can be adjusted, the next step will be to examine the NO_2/NO ratio as a function of $[O_3]$ and $[NO_y]$. The NO_2/NO ratio is controlled by several physical and chemical parameters that limit reasonable values to relatively narrow ranges depending on the conditions. For example, in sunlit atmosphere we expect the NO_2/NO ratio to fall between 2 and 6. We expect the ratio to increase as a function of ozone. Finally we will examine the time series of the NO_x/NO_y ratio. Fresh pollution will yield an NO_x/NO_y ratio close to 1, while aged pollution will tend toward zero. If the data behave as expected, based on an understanding of the attendant atmospheric dynamics, this ratio could be very useful in elucidating processes that lead to particle formation by establishing the photochemical age of an air mass..

Next, the other NO_y species measured (PAN, HNO_3, particulate nitrate) will be examined in both time series and as their contribution to NO_y. This examination of the reactive nitrogen reservoir can be helpful in describing the dynamic and chemical history of an air mass (Buhr et al., 1990; Trainer et al., 1991). Time series analyses for each of the NO_y species will be performed. Finally, the ratio $\Sigma NO_{y(i)}/NO_y$ will be examined to determine the overall consistency of the reactive nitrogen species data set.

Further analysis would incorporate other chemical and physical parameters as needed to generate a better understanding of the conditions that lead to formation of nitric acid and, subsequently, particulate nitrate. It is expected that the conditions identified will also vary as a function of meteorological conditions.

Scope of Work

The individual task elements involved in Task 1.1b include

1. Compile the coincident measurements of NO_y and NO_y species collected at the anchor sites. Integrate the faster measurements over the collection period of the slower measurements where applicable.
2. Evaluate the consistency of the collocated NO_y measurements for the Sierra Nevada Foothills, Angiola, and Fresno sites.
3. Evaluate the data quality of the NO_2 measurements and the NO_x ($NO+NO_2$) quantity for the data collected at all the anchor sites.
4. Evaluate the data quality of the PAN measurements for the data collected at all the anchor sites.
5. Evaluate the data quality of the HNO_3 measurements for the data collected at all the anchor sites.
6. Summarize the partitioning of NO_y among the NO_y species as a function of time of day and as a function of air mass age (given as NO_x/NO_y when possible).
7. Assess the quality of the measurements within the stated measurement uncertainties.
8. Examine the NO_y partitioning as a function of ozone, PM, meteorological conditions, and season.
9. Prepare technical memorandum discussing these technical elements and results of analysis.

Time Line

STI shall complete task elements 1 through 6 before June 6, 2003. A draft technical memorandum will be presented to ARB at that time. Any necessary revisions to the technical memorandum after review by ARB will be completed four weeks after receipt of comments.

Schedule of Deliverables

Deliverable	Deliverable Due Date
Draft technical memorandum	June 6, 2003
Final technical memorandum	Four weeks after ARB comments on draft
Manuscript for publication/presentation	Fall 2003

Description of Deliverable(s)

The technical memorandum will include

- A discussion of the data included in the evaluation of the reactive nitrogen partitioning,
- An evaluation of the consistency of the collocated NO_y measurements for the Sierra Nevada Foothills, Angiola, and Fresno sites,
- An evaluation the data quality of the NO_2 measurements and the NO_x ($NO+NO_2$) quantity for the data collected at all the anchor sites,
- A summary of the partitioning of NO_y among the NO_y species as a function of time of day and as a function of air mass age (given as NO_x/NO_y when possible).
- An assessment of the quality of the measurements within the stated measurement uncertainties, and
- An examination of the NO_y partitioning as a function of ozone, PM, meteorological conditions, and season.

All of the appropriate data plots prepared to conduct the above analyses will be included as well.

ARB Staff Assigned to This Task

The ARB Project Manager assigned to this Task is

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STI Staff Assigned to This Task

The STI Project Manager is Lyle R. Chinkin. The STI Task Manager assigned to Task 1.1b is Martin Buhr.

Percentage of Work, Data Products to be Performed/Delivered by ARB

None.

Software and Models to be Used by STI

The following software will be used in Task 1.1b:

- IGOR Pro version 4 (Wavemetrics, Inc.) will be used for data analysis and manipulation.
- Microsoft Word will be used in preparing documentation.

Models, Reports, or Other Data to be Supplied to STI by ARB

STI will use the Central California Air Quality Studies (CCAQS) database as the primary data for all comparisons and evaluations.

References

Buhr M.P., Parrish D.D., Norton R.B., Fehsenfeld F.C., Sievers R.E., and Roberts J.M. (1990) Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site. *J. Geophys. Res.* **95**, 9809-9816.

Trainer M., Buhr M.P., Curran C.M., Fehsenfeld F.C., Hsie E.Y., Liu S.C., Norton R.B., Parrish D.D., Wiliams E.J., Gandrud B.W., Ridley B.A., Shetter J.D., Allwine E.J., and Westberg H.H. (1991) Observations and modeling of the reactive nitrogen photochemistry at a rural site. *J. Geophys. Res.* **96**, 3045-3063.